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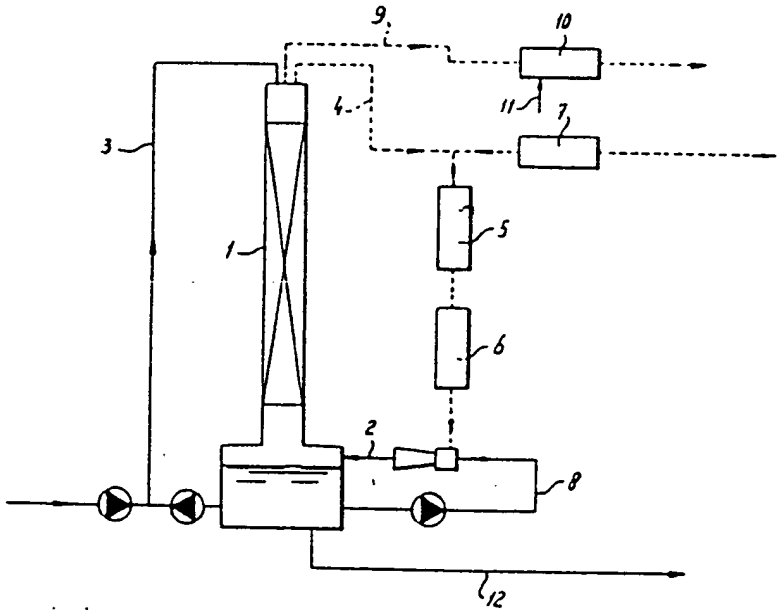

(57) Abstract

A process is provided for the purification of water which is contaminated with environmentally undesirable components, such as halogenated hydrocarbons, wherein the contaminated water or the gaseous and/or liquid components present therein or derived therefrom are subjected to at least two of the following treatments: treatment with ozone, treatment with UV radiation, treatment with a solid catalyst. A combined treatment with ozone and a solid catalyst, such as activated carbon, is preferred. An apparatus for a cocurrent or countercurrent realisation of the purification process is also provided. The apparatus can comprise one or more purification reactors.

* See back of page

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Process and apparatus for the purification of contaminated water by activated ozone

This invention relates to a process for the purification of water contaminated e.g. with halogenated hydrocarbons, with activated ozone. The contaminated water may come available as groundwater from waste deposits, but also as direct effluents from household activities, urban conglomerates and industries.
From an environmental point of view, such effluents cannot be discharged without a thorough purification. Most current technologies like concentration/incineration, wet air oxidation, biotreating etc., have distinct disadvantages. They are either not economically viable, generate secondary waste problems or do not achieve sufficiently low residual concentrations for environmentally acceptable solutions.

The invention provides a solution for the above mentioned problems. It is applicable to a variety of toxic components in waste streams like halogenated hydrocarbons, including chlorine and bromine containing compounds, dioxines and PCB's, pesticides, insecticides, (polycyclic) aromatics, cyanides, (glycol) esters, organic acids, alcohols, hydrocarbons, etc., as well as micro-organisms.

The process according to the invention can be applied in the vapour phase (volatile components) as well as in the liquid phase. In both cases the active reagents are assumed to be oxidative radicals derived from activated ozone either by short wave UV radiation or by a solid catalyst.

If UV radiation is applied at a wavelength below 200 nm, and preferably at 185 nm, ozone can be produced from oxygen containing gas as well. At a wavelength in excess of 200 nm, and more specifically at 245 nm, UV radiation only activates ozone but does not produce additional ozone.

As the catalyst, a number of solid components can be used. Good results have been obtained using activated carbon (surface area 400-800

m2/gram). Alumina and silica can also be used. In general, solid components and mixtures thereof can be used which have an absorption capacity or affinity to the toxic component to be treated as well as to ozone. In practice, the solid catalyst should have a surface area of at least 50 m^2/gram and a pore volume greater than 0.1 cm^3/gram. The activity of the catalyst can be improved by doping with (transition) metals like copper, iron, molybdenum, cobalt, etc.

In the vapour phase the reactions take place very fast (within a few seconds at ambient temperature). In the liquid phase, ozone is injected through a diffusor or an injection system such as a venturi; the reaction proceeds much slower than in the vapour phase. For many applications a combination of gas treatment and liquid phase treatment is favourable.

Because the reaction proceeds reasonably fast at ambient temperature, higher temperatures are usually not required. However, treatment at higher temperatures is feasible and often preferable, in particular when a solid catalyst is applied.

As a particular embodiment of the process according to the invention contaminated water is purified by treating it with at least a solid catalyst, such as activated carbon, and the catalyst is continuously or semi-continuously regenerated with ozone.

The invention can be conducted in several types of equipment e.g. co-current (liquid and ozone gas in the same direction) or countercurrent in a stripping tower.

A co-current equipment is illustrated in Figure 1. The apparatus consists of 1-10 reactors in series and was used for purifying the groundwater of the Volgermeerpolder in The Netherlands. The conversions obtained with ozone/UV in the liquid phase and with ozone/active carbon in the vapour phase are given in Table 1. It will be seen that e.g. a toxic component like monochlorobenzene is degraded with an efficiency of 99.99% The products were mainly water, carbon dioxide and NaCl (after neutralization of the HCl formed).

Table 1

GROUNDWATER PURIFICATION

VOLGERMEERPOLDER

contaminant	influent level (ppb)	effluent level (ppb)	local limits for discharge on surface water (ppb)
monochlorobenzene	7900	1.0	1.0
chlorophenols	500	0.3	1.0
EOCl	810	3.3	5.0
polycyclic aromatics	40	0.6	1.0
naphthalene	25	0.5	1.0
phenol	27	0.5	1.0
alkylphenols	320	0.2	1.0
benzene	1400	0.5	1.0

In the apparatus according to the invention, a variety of toxic components can be degraded. The apparatus consists of from 1 up to 10 reactors (100, 200, 300, ...) which can be columns packed with solid fillings or solid catalysts. The said reactors have a contaminated water supply (101, 201, 301, ...), a water discharge (102, 202, 302, ...) and a gas discharge (103, 203, 303, ...); further, the reactors (100, 200, 300, ...) are equipped with a recycle supply (104, 204, 304, ...) for ozone containing liquid and a recycle discharge (105, 205, 305, ...) for ozone depleted liquid, whereby a UV treating unit (106, 206, 306, ...) and/or an ozone supply (107, 207, 307, ...) can be included between the recycle supply (104, 204, 304) and the recycle discharge (105, 205, 305, ...).

The gas discharge (103) which is connected to a UV treating unit (108), and/or the gas discharge (109) of UV treating unit (108) is fed to a venturi (110) incorporated in a liquid recycle loop (111), which loop is connected to a reactor (100). In the liquid recycle loop (111), an electromagnetic water treatment installation (112) for eliminating metals such as iron or calcium, can be incorporated.

The ozone supply (107, 207, 307, ...) can advantageously be provided via an injection system such as a venturi (116, 216, 316, ...) connected

to the water recycle loop (104, 204, 304, ...).

As a result of intensive mixing of ozone (gas) and water as well as as a result of the presence of r cycle loops, the reactions take place both in the water phase and in the vapour phase. After the ozone treatment, the residual gases are purified by an "active filter" (114) containing a solid catalyst as specified above. If necessary, additional ozone can be added just before the catalyst layer.

The purified gases can be discharged into the air (121) and the purified water can in general be discharged (122) onto local surface water.

The invention can also be applied countercurrently. The apparatus (Fig 2) comprises a stripping tower (1) having a supply (2) for gas and/or gas containing liquid on the lower side, and on the upper side both a liquid supply (3) and a gas discharge (4) which is connected to a UV treating unit (5, 6) and to an ozone supply unit (7). The discharge of the UV treating unit(s) (5, 6) is connected to a liquid supply (2) of a recycle loop (8). A stripping tower is particularly advantageous when the majority of the toxic components are volatile and the heavy components can be oxidized relatively easily. In that case, a single stripping tower will be sufficient, but 2-5 towers can be used as well. The gases leaving the tower (9) may contain residual toxic components. These can be degraded with additional ozone (11) in a separate reactor (10) containing a solid catalyst as specified above. Also in the stripping tower the use of catalyst rather than a conventional filling material will in most cases be preferable.

The stripping tower as described in figure 2 was applied for purifying an industrial waste stream containing 7.431 mg/l of dichloromethane. It was shown that by adding sufficient caustic soda to neutralize the HCl formed and by using ozone/UV as the oxidizing agent, the effluent contained 68 mg/l only, thus achieving a conversion of 99.1%. By using active carbon and silica as a catalyst in combination with ozone, a conversion of 99.9% was achieved.

The invention is based on a catalytic oxidation process, which can be applied homogeneously (UV) or inhomogeneously (solid catalyst), or as a combination of homogeneous and inhomogeneous steps. The choice of the equipment is mainly determined by the reaction parameters and reaction kinetics of individual toxic components to be removed. Therefore, the apparatus described hereabove is only by way of an example, and various modifications of the apparatus can be contemplated within the scope of the present invention.

CLAIMS

1. Process for the treatment of water which is contaminated with undesirable components, such as halogenated hydrocarbons, by subjecting the contaminated water or the gaseous and/or liquid components present therein or resulting therefrom to at least two of the following treatments:
- treatment with ozone;
- treatment with UV radiation;
- treatment with a solid catalyst.

2. Process according to claim 1, wherein treatment with ozone is applied in combination with a solid catalyst.

3. Process according to claim 1 or 2, wherein activated carbon, alumina and/or silica is used as a catalyst.

4. Process according to any of claims 1-3, wherein a catalyst having a surface area of at least 50 m^2/gram and a pore volume of at least 0.1 cm^3/gram is used.

5. Process according to any of claims 1-4, wherein the ozone is produced by subjecting oxygen containing gas to UV radiation having a wavelength of less than 200 nm, particularly around 185 nm, or by means of an electric discharge.

6. Process for the treatment of contaminated water comprising treatment with a solid catalyst, wherein the catalyst is continuously regenerated with ozone.

7. Apparatus for conducting the process according to any of claims 1-6, comprising one or more reactors (100, 200, ...) optionally packed with a solid catalyst, said reactors being euipped with a contaminated water supply (101, 201, ...), a water discharge (102, 202, ...) and a gas discharge (103, 203, ...), a recycle supply (104, 204, ...) for ozone containing liquid and a recycle discharge (105, 205, ...) for ozone depleted liquid.

8. Apparatus according to claim 7, wherein a UV treating unit (106, 206, ...) and/or an ozone supply (107, 207, ...) is provided between the recycle supply (104, 204, ...) and the recycle discharge (105, 205, ...).

9. Apparatus according to claim 8, wherein the ozone supply (107, 207, ...) is connected to the water recycle loop (104, 204, ...) via an injection system such as a venturi (116, 216, ...).

10. Apparatus according to any of claims 7-9, wherein the gas discharge (103, ...) is connected, optionally via a UV treating unit (108) and/or a gas discharge (109), to a venturi (110) incorporated in a liquid recycle loop (111), which loop is connected to a reactor (100).

11. Apparatus according to any one of claims 7-10, wherein the discharge (103, 203, ...) is connected to an active filter (114) containing a solid catalyst having a surface area of at least 50 m^2/gram and a pore volume of over 0.1 cm^3/gram.

12. Apparatus for conducting the process according to any of claims 1-6, comprising a stripping tower (1) having a supply (2) for gas and/or gas containing liquid on the lower side, and on the upper side both a supply for the liquid to be treated (3) and a gas discharge (4) connected to a UV treating unit (5, 6) and to an ozone supply unit (7), whereby the discharge of the UV treating unit(s) (5, 6) is optionally connected to the supply (2) of the stripping tower (1), and the supply (2) can be part of a recycle loop (8).

13. Apparatus according to claim 12, wherein a solid catalyst is contained in the stripping tower (1) and/or in a unit (10) for treating the residual gas stream (9), which unit is connected to an ozone supply (11).

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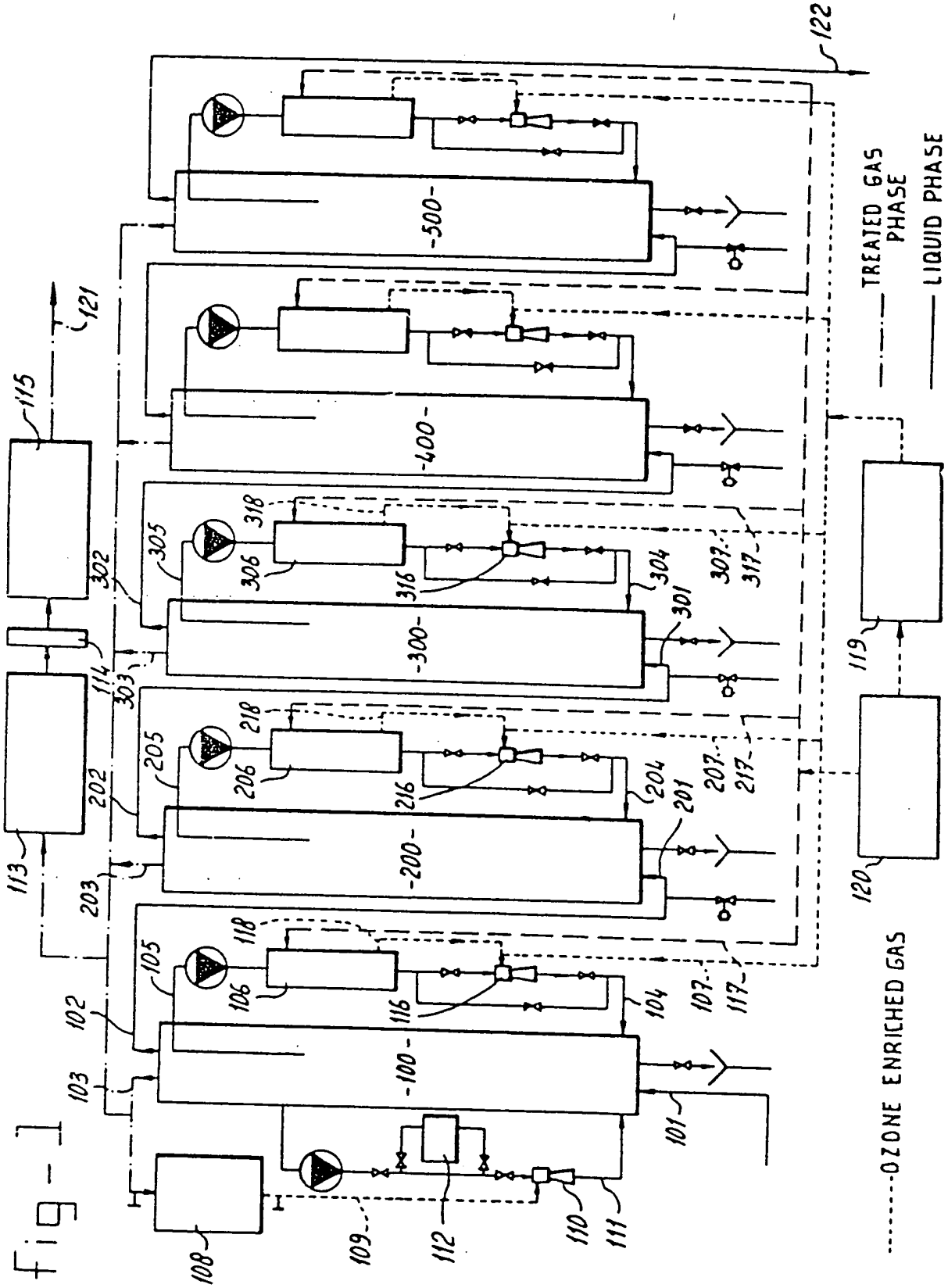
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TREATED GAS PHASE
LIQUID PHASE
OZONE ENRICHED GAS

Fig - 1

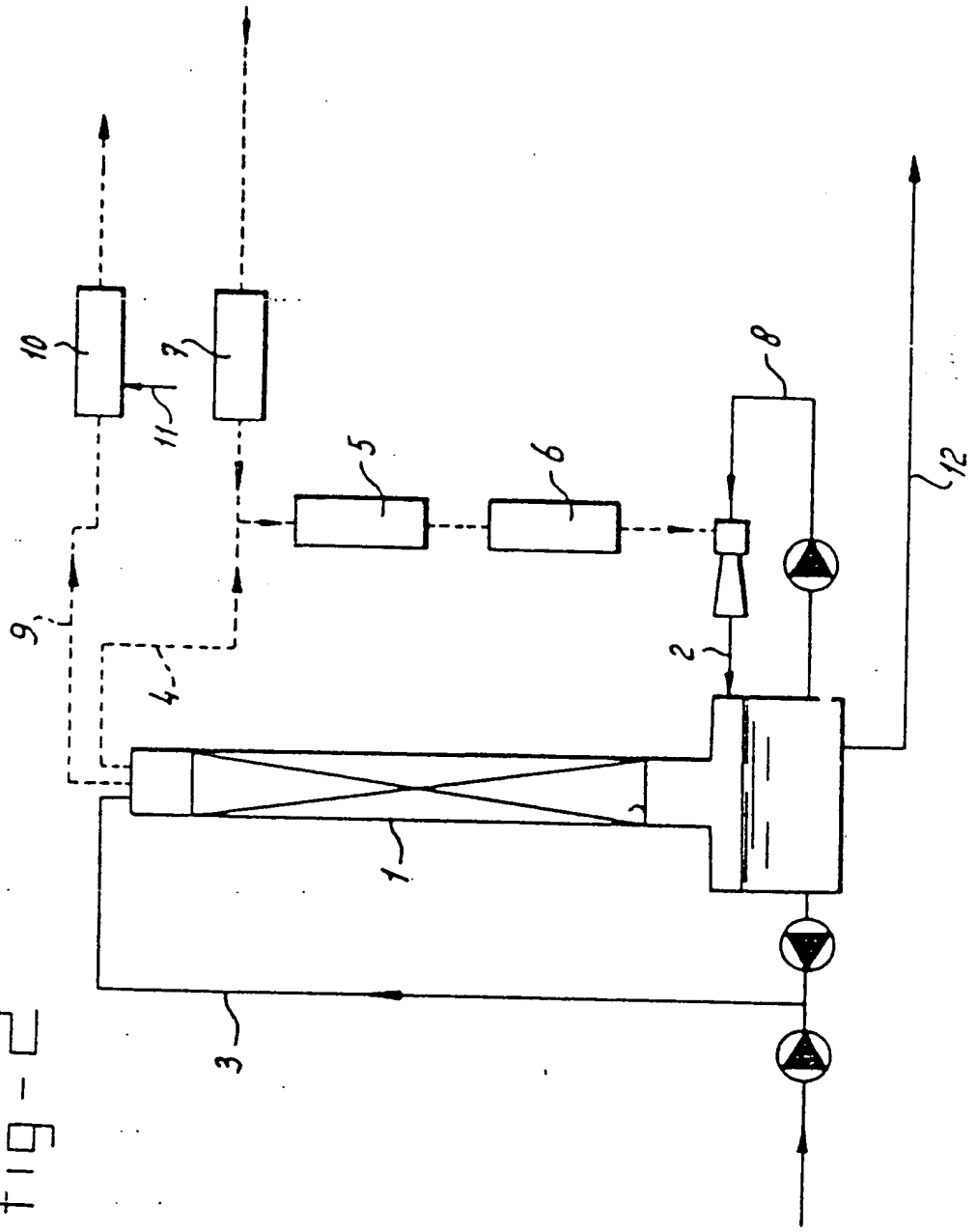

Fig - 2